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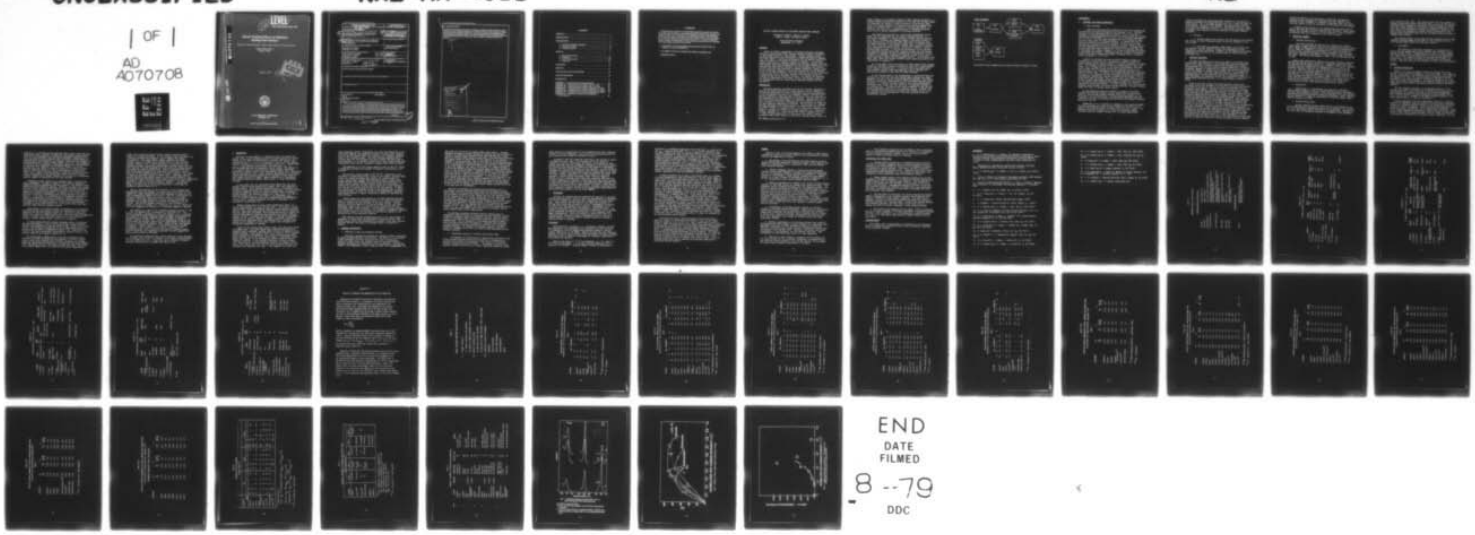

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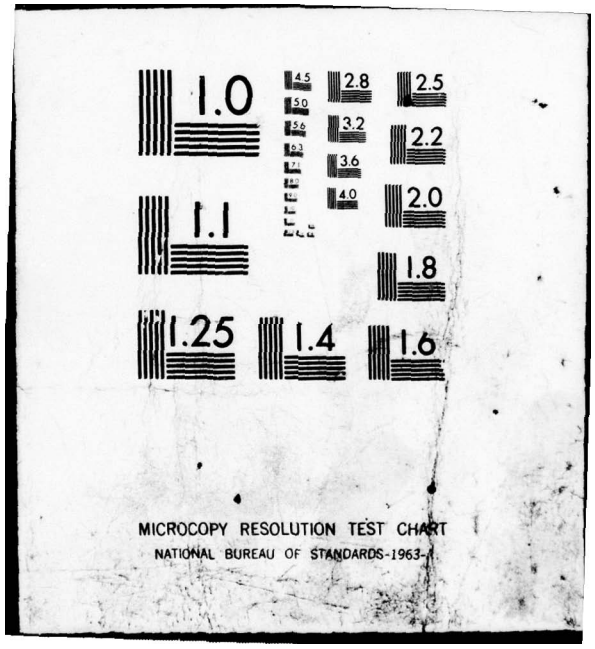
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Solvent Cleaning Effects on Miniature Bearing Steel Surfaces

MARIANNE K. BERNETT, BARBARA J. KINZIG, JAMES S. MURDAY, AND HAROLD RAVNER

Surface Chemistry Branch
Chemistry Division

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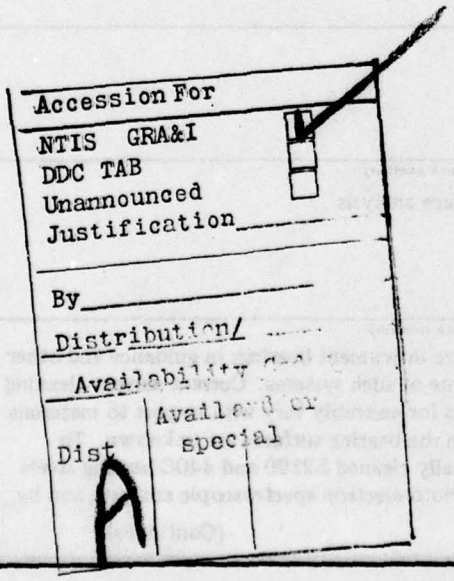
wettability and infrared studies; they were then subjected to standard sequential cleaning cycles and to individual solvents at several Navy facilities, and re-examined at NRL by the same techniques. The data indicated that various quantities of hydrocarbon, ester, and other residues were deposited during the cleaning process on the reference surfaces. The results are discussed in terms of comparisons of the types, levels, and probable origins of the contaminants, and their implications regarding bearing life and reliability.



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FOREWORD

The maintenance procedure for aircraft bearing assemblies specified in NAVAIR 01-1A-503 permits variation in bearing cleaning solvent, sequence and methods (e.g. ultrasonic, spray, dip) of processing. Since findings have shown that detrimental effects can result from solvent cleaning of steel bearing surfaces, work was initiated by the Naval Air Systems Command (AIR-4114C, Mr. A. J. Koury) to assess the impact of residual contaminants in terms of bearing performance, life and reliability. The initial findings presented herein include:

1. A description of cleaning processes including method, solvent, cycle, and filtration for each NAVAIREWFAC.

2. An analysis of solvent and bearing metal surface contaminants, and

3. Wettability results.

SOLVENT CLEANING EFFECTS ON MINIATURE BEARING STEEL SURFACES

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ABSTRACT

Traces of surface contaminants on precision miniature instrument bearings in guidance and other critical systems can greatly contribute to the ultimate failure of such systems. Current solvent-cleaning procedures employed by Navy facilities to prepare bearings for assembly vary with respect to materials and methods, but the specific effects of these variations on the bearing surfaces are unknown. To critically examine these effects, reference surfaces of specially cleaned 52100 and 440C bearing steels were characterized at NRL by Auger electron and X-ray photoelectron spectroscopic analysis, and by wettability and infrared studies; they were then subjected to standard sequential cleaning cycles and to individual solvents at several Navy facilities, and re-examined at NRL by the same techniques. The data indicated that various quantities of hydrocarbon, ester, and other residues were deposited during the cleaning process on the reference surfaces. The results are discussed in terms of comparisons of the types, levels, and probable origins of the contaminants, and their implications regarding bearing life and reliability.

INTRODUCTION

Precision miniature instrument bearings are critical components of aircraft and marine guidance and related systems, and the presence of even minute quantities of surface contaminants can result in malfunction or even catastrophic failure of the component systems. Effective preparative cleaning of these bearings is therefore a critical operation in the assembly and the maintenance of such systems. Bearings sent to the Naval Air Rework Facilities (NARF) for rework and cleaning (1) arrive with a variety of lubricants, contaminants, and histories of storage and use under generally unspecified conditions. The procedure for cleaning bearings specified in the bearing manual (2) permits some latitude for each NARF to modify its cleaning cycle to its individual preference with respect to sequence of solvents and methods employed, e.g., ultrasonic, dipping, spraying, etc. Some previous NRL studies (together with the C. S. Draper Research Laboratory) (3) have shown that surface cleaning procedures could induce surface alterations of bearing steels; little is

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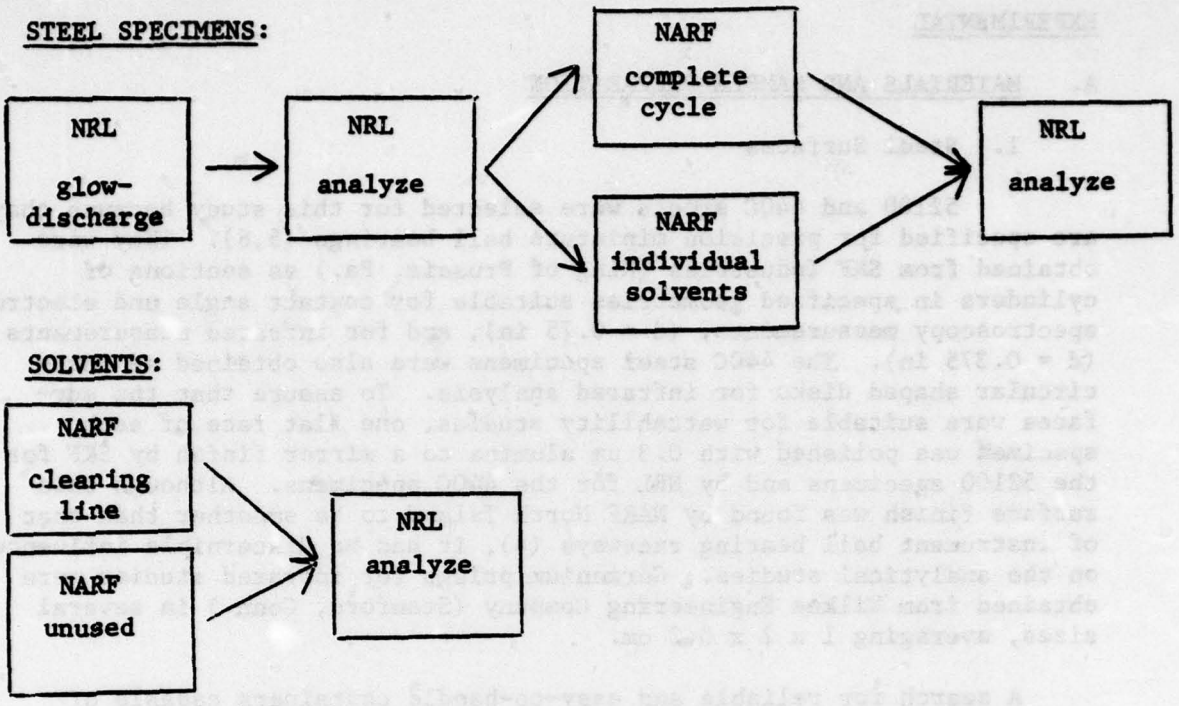
known, however, of the specific effects of NARF cleaning procedures. A research program was therefore sponsored by the Naval Air Systems Command to investigate the effects of these procedures on the surface composition and surface chemistry of bearing steels; specific emphasis was given to the implications of the results on bearing performance, reliability, and life, and to recommendations for cleaning procedures which could be readily implemented in existing facilities.

The program was conceived as a joint effort between NRL and the NARFs. NRL was responsible for the surface chemistry studies: a) wettability phenomena; b) surface analysis by Auger electron spectroscopy (AES) to determine the elements present on the metal surface; c) X-ray photoelectron spectroscopy (XPS) which gives information about the chemical species of the elements present; and, d) Infrared attenuated total reflectance spectroscopy (IR-ATR) which chemically analyzes trace quantities of surface species, especially if organic. The individual NARFs provided: a) facilities and manpower to process metal test specimens through their normal cleaning routine and such special procedures as requested by NRL; b) samples and specifications of their solvents for subsequent "fingerprint" analysis at NRL; and c) information relevant to safety and environmental factors. In addition to the above input, NARF North Island provided primary engineering support and consultation as required (4).

All of the NARFs (with the exception of NARF Alameda whose cleaning system was inoperative during the period set aside for it) participated in the study as reported below. It should be noted that NARF Cherry Point normally reworks larger bearings only, and is therefore not specifically equipped to deal with instrument bearings.

In this initial phase of the investigation, a controlled study was carried out on 52100 and 440C steel blanks whose surfaces were representative of those of actual precision miniature bearings. The metals, specially cleaned and characterized by NRL as reference surfaces, were subjected to a complete cleaning process at each participating NARF; individual steel blanks were also subjected to individual solvents in the cleaning line. The surfaces were then re-analyzed at NRL and each surface composition compared to the reference surface. Solvents from the cleaning line during actual processing and solvents prior to use, "as received from the manufacturer," were also analyzed at NRL for contamination content.



The present report summarizes the research results obtained to date.

EXPERIMENTAL

A. MATERIALS AND SAMPLE PREPARATION

1. Steel Surfaces

52100 and 440C steels were selected for this study because they are specified for precision miniature ball bearings (5,6). They were obtained from SKF Industries (King of Prussia, Pa.) as sections of cylinders in specified geometries suitable for contact angle and electron spectroscopy measurements, (d = 0.75 in), and for infrared measurements (d = 0.375 in). The 440C steel specimens were also obtained as semi-circular shaped disks for infrared analysis. To assure that the surfaces were suitable for wettability studies, one flat face of each specimen was polished with 0.3 μm alumina to a mirror finish by SKF for the 52100 specimens and by NRL for the 440C specimens. Although this surface finish was found by NARF North Island to be smoother than that of instrument ball bearing raceways (4), it had no discernible influence on the analytical studies. Germanium prisms for infrared studies were obtained from Wilkes Engineering Company (Stamford, Conn.) in several sizes, averaging 1 x 2 x 0.2 cm.

A search for reliable and easy-to-handle containers capable of maintaining a contamination-free atmosphere for sample storing and shipping proved glass or metal vessels to be either inadequate or cumbersome. Polyethylene cylindrical boxes with hinged snap-fit lids (Cole Parmer, Inc., Chicago) met all of the desired requirements; they were easy to handle and XPS studies showed that there was little or no deterioration of the cleanliness of glow-discharged specimens stored in them for several days. To prevent the specimen surfaces from contacting the walls of the container and thus acquiring accidental and unwanted contamination, methods were devised to immobilize the samples. For the large 52100 steel specimens, fine stainless steel mesh (120/inch) was cut into collars and crimped between sample circumference and container; for the smaller 52100 specimens and Germanium prisms, the retainers consisted of square mesh baskets. All 440C specimens were fitted inside machined Teflon collars; set screws allowed sufficient clearance between sample and collar to prevent direct contact.

All specimens were initially cleaned by sequential ultrasonic cleaning with absolute ethanol, acetone (Fisher ACS, certified) and Freon 113 (from an NRL multiply-distilled high purity supply, and re-distilled in an all-glass still). The 440C steel specimens were then passivated according to specification MIL-B-81793 with sodium dichromate and nitric acid (5).

Immediately prior to analysis or transport to the respective NARFs, the steel specimens were again solvent-cleaned and the mesh collars, baskets, and germanium samples refluxed in Freon 113 for 2 hours. The specimens were then processed in a plasma glow discharge chamber (Harrick Scientific Company, Ossing, N.Y.) to assure reproducible

reference surfaces free from carbonaceous residues (7); the glow discharge was provided by nitrogen gas and a low (3 to 5 watt) RF level for 45-60 minutes. Up to six large specimens and their collars could be simultaneously processed in the chamber. Upon removal from the chamber each sample was immediately sealed in its polyethylene container, where it remained until required for either analysis or the NARF cleaning procedure.

2. Solvents

a. Solvent samples were obtained from the tanks in the cleaning line during the actual cleaning process, as will be indicated in the next section.

b. Each NARF also supplied to NRL unused, "as received from the supplier," solvent samples together with information on their shipping and storage containers. Analysis of such samples would provide information on the purity of the solvents prior to their use in the processing line.

B. SAMPLING PRODEDURES

The metal specimens used in this first phase of the project were handcarried by NRL personnel in the polyethylene containers described above to each NARF to determine whether the specimens would remain uncontaminated under the most careful shipping conditions, and whether subsequent shipment by commercial air freight would also be acceptable. It was also desired to acquaint the personnel with the cleaning practices at each NARF. Since each NARF was visited at random times, the specimens were in contact with some solvents in different stages of their replacement or reclamation cycles; the contamination levels of the exposed metal specimens was thus, to a certain extent, a matter of chance.

Prior to the North Island and Norfolk sampling, freshly glow discharged 52100 steel specimens were analyzed by electron spectroscopy, the results to be used as controls and base-line references for all subsequent 52100 samples. Reference data for freshly glow discharged passivated 440C steel specimens were obtained at a later date. 52100 steel specimens were used in the North Island, Norfolk, Jacksonville and Pensacola studies and 440C passivated specimens in Cherry Point. Table I shows the sampling plan for all participating NARFS. Some transit control samples were carried and returned unopened in their containers to provide a data baseline for each NARF; other control samples were opened only to the atmosphere of the NARF cleaning facility for the duration of the cleaning cycle to provide information on the contamination from that atmosphere. Samples subjected to the cleaning materials (Appendix I) in the complete cleaning cycle used at the respective NARF for miniature precision (oil-lubricated) bearings (Appendix II a-e) provided the most significant information on that cleaning procedure. Such samples were returned either in: a) NRL containers, or b) in packages of the same types of antistatic (AS) polyethylene or Nylon bags used by the NARFs for shipping or storing bearings; the latter samples

yielded information on the protection or additional contamination acquired by such packaging (8). Specimens were also exposed to individual solvent treatments to determine contaminant types and levels from each solvent as well as the effect of each solvent on the surfaces.

A sample of each solvent in the cleaning line was taken from its tank at the same time the steel specimens were processed. These solvent samples were returned to NRL for infrared analysis to detect possible correlations with the contaminants on the steel surfaces.

C. ANALYTICAL METHODS

1. Electron Spectroscopy:

Each steel specimen was analyzed for elemental and chemical constituency by Auger electron (AES) and X-ray photoelectron spectroscopy (XPS). Auger and XPS spectra can detect and identify all elements above He to a depth of 5-30Å and in concentrations to small fractions of a monolayer. More detailed chemical bonding information can be obtained from subtle changes in peak shapes or energy shifts in high resolution XPS scans. The typical area sampled is about 1 mm^2 for XPS and 0.01 mm^2 for AES.

Spectra were taken with a Physical Electronics Industries combined XPS/AES spectrometer using a double pass cylindrical mirror analyzer. XPS spectra were recorded using Al $K_{\alpha 1,2}$ radiation (1486.6 eV). Binding energies (BE) were referred to the measured XPS $Au_{4f7/2}$ line at the published standard of 83.8 eV (9); reproducibility of the Au BE was $\pm$ 0.2 eV. The 3 KeV electron beam for AES was maintained at 11 μA. The spectroscopic analytical approach for any one selected area of each specimen was: a) a full XPS spectrum to observe elemental species; b) high resolution XPS spectra for selected peaks, e.g., Fe, O, C, S, N and other identified elements of specific interest, to determine their abundance and chemical state; c) a full AES spectrum, taken last to avoid possible electron beam damage affecting the XPS results.

2. Wettability:

Contact angle (Θ) measurements were made with a Rame-Hart contact angle goniometer using the slowly advancing sessile drop method (10) with three diagnostic liquids: triply distilled water, and carefully purified and percolated methylene iodide and hexadecane. Each Θ reported was the average of at least two measurements on separate sessile drops, taken in room air at 20-25°C.

3. Infrared Spectroscopy:

Fourier transform infrared (FTIR) spectra were obtained at the Norfolk NARF Materials Engineering Laboratory, at Digilab, Inc., Columbia, Md. or at Case Western Reserve University, Cleveland, Ohio. Residues on the solid steel and germanium specimens were examined in the attenuated

total reflection mode (ATR). Each surface under study was clamped to a multiply reflecting infrared transparent KRS-5 crystal and the spectral information thus obtained by the several traverses through the residue layer was further enhanced by the multiple scanning capability of the FTIR. Data for the specimens processed at Jacksonville, Pensacola, and Cherry Point were obtained on a Digilab FTS-14 spectrometer at Case Western Reserve University where the ATR attachment produced spectra of somewhat lower quality.

The infrared spectra of the liquid solvents obtained from the NARF cleaning processing tanks were obtained in the transmission mode in a 0.025 mm path length liquid cell with AgCl windows.

4. Gravimetry:

The levels of non-volatile components in the unused "as received from the manufacturer" solvent samples were considered as one measure of their purity. Weighed amounts of solvent in glass beakers were evaporated at 70°C and maintained in an oven at that temperature for 2 hours. The original solvents and residues were weighed to an accuracy of 0.1 mg, with the residue content reported in parts per million. Reported values are the average of at least two determinations.

RESULTS

A. ELECTRON SPECTROSCOPY

Tables II a-e list the elements detected by AES and XPS on the surface of each specimen processed at the various NARFs. Also shown are the peak intensities of the elemental signals normalized with respect to the signals of Fe (Fe = 10), but uncorrected for the AES or XPS sensitivities to the various elements. Although uninformative as to the actual quantities or percentages of each element present in the surface, these ratios provide useful comparisons among the different specimens examined.

The main elements observable in all specimens were Fe, O (the surface iron oxide), and C whose line intensity and positions are the key indicators of the amount and type of C-containing contaminants. Other elements detected on various specimens in trace amounts were S, Cl, N, Zn, Ba, and F. Signals of the minor component elements of the steel alloys, such as Cr, were not considered.

Several specimens in the early experiments (Table II a) revealed traces of Ba suggesting possible residues of barium dinonyl naphthalene sulfonate, a corrosion inhibitor present in the preservative lubricant used by the vendor in shipping. After repolishing the specimens to remove the surface contaminants, the Ba signals were negligible. S and Cl are common atmospheric contaminants, which accounted for their higher levels on some transit opened specimens; however, larger amounts were also detected on specimens after selected solvent treatments. The line

position of S in the XPS spectra indicated that it was in the form of an oxide rather than a sulfide. Solvents that contributed large traces of S and Cl on the specimens also contributed measurable quantities of N, e.g., the tanks of Freon ultrasonic (US) at Norfolk, trichlorethane at Jacksonville or final naphtha 3 at Pensacola, indicating the presence of some contamination in these solvents (Tables II b,c,d). The presence of Zn cannot as yet be explained. Significant amounts of F were deposited by the Freon vapor degreaser (VD) at Norfolk (Table II b) on one specimen only, and lesser but definite traces of F by Freon US tanks 1 and 2 at Pensacola (Table II d) and trichlorethane at Cherry Point (Table II e). Since F deposits cannot be caused by the volatile Freon itself, the presence of the element must result from either a less-volatile, high-molecular-weight component of the Freon or a fluorinated impurity capable of adsorbing onto the steel specimen.

Ubiquitous organic vapors in the atmosphere make C the most prevalent contaminant. The small C signals on the controls indicated a minimum of handling contamination during transfer to the XPS-AES vacuum system after glow discharge cleaning. Similarly low levels of C, along with low S and Cl levels, on the unopened transit samples confirmed the efficacy of the polyethylene transport containers in protecting the samples from airborne contaminants. XPS spectra of Fe, O and C representative of relative intensities after various exposures are shown in Figure 1: a low level of C contamination is represented in Figure 1a. These low contamination levels also provided a reference point for subsequent levels acquired during the various cleaning procedures; with the exception of the samples subjected to Freon and trichloroethane treatment at North Island (Table II a), these latter levels were generally much higher than the reference levels.

Large amounts of C generally appear as overlayers on the specimens; when thick enough, these layers can mask the underlying Fe and O and suppress their spectral signals (Figure 1c). Use of the resulting Fe signals as a basis for normalizing the data would then cause an exaggeration of the C overlayer constituent with respect to the other substrate elements; overall trends, however, would still be apparent.

To obtain semiquantitative element abundance ratios, the observed XPS peak intensities, I_i, were corrected according to their relative sensitivities (Appendix III) and are listed as I^N_{Fe}, I^N_O and I^N_C in Tables III a-f. The normalized intensities I^N_i can be interpreted as being valid within the limits of homogeneous surface film. Comparison of I^N_O and I^N_C to I^N_{Fe} yields approximate stoichiometric elemental ratios in the surface; these are also shown in Tables III a-f.

The stoichiometric I^N_O/I^N_{Fe} ratios in the glow discharged control 52100 and 440C steel surfaces were approximately 5.5 and 8.0, respectively; these ratios remained fairly constant throughout all specimen exposures, and constituted essentially the substrate iron oxide (Appendix III). The I^N_C/I^N_{Fe} ratios in the control surfaces were small, less than 1 and slightly higher than 1 in 52100 and 440C steels, respectively.

Larger ratios therefore indicate surface deposits acquired during transit or cleaning processing. For the unopened transit specimens, the C fraction increased only slightly, barely changing the surface stoichiometry. The opened transit samples generally had higher C contents, usually in tandem with increased traces of other airborne elements (Tables II a-e). Marked increases in C occurred with the specimens processed through the complete NARF cleaning cycles, with the least increase for those processed at North Island and Jacksonville and the largest for those at Cherry Point. Heavy C overlayers were laid down on specimens processed with individual "solvents-only," such as Freon US, trichloroethane and Freon VD at Norfolk, naphtha 1 and 2 tanks at Pensacola, and every solvent at Cherry Point. Conversely, several solvents deposited only minimal amounts of carbonaceous material, e.g., Freon US and trichloroethane at North Island, Freon US and VD at Jacksonville, and Freon US (tank 2) and final naphtha at Pensacola. All other specimens had C present in varying but moderate amounts. A significant I^N_F/I^N_{Fe} ratio was noted in one specimen subjected to Freon vapor degreasing at Norfolk (Table III b).

The C_{1s} line positions of the XPS spectra of all specimens were predominantly those of aliphatic C-C bonds, with a BE of 285.0 eV (11), (Figure 1a), whose intensitites were those expressed in Tables III a-f. Small but measurable signals with a BE of $\tilde{}$ 289.0 eV, characteristic of carboxy $C^{=O}_{-O}$ bonds (12) were also detected (Figure 1 b,c) in many specimens. The signal intensities of these carboxyl-containing contaminants were at times masked by overlayers of aliphatics from the solvents. One Norfolk specimen subjected to Freon VD showed a C_{1s} signal at BE 291.6 eV (Figure 1 b), indicative of a CF_2 or a CF_2Cl bond (11) which suggested the presence of a fluorinated compound or polymer.

The dominant O_{1s} signal on all specimens examined occurred at a BE of $\sim$530.5 eV (Figure 1a,b), attributable to iron oxide (13). For several specimens a broadening of line width (Figure 1 c) or a shoulder at a higher BE indicated additional oxygen linkages; these signals are characteristic of organic compounds where the oxygen is linked as alcohol, carbonyl or ester (14). Such a broadening was evident on the Norfolk Freon US specimen; definite shifts toward higher O energy were found on all Cherry Point samples, which, along with the large amounts of aliphatic C signals (Figure 1 c), gave definite proof of organic contaminants, such as esters, in that series. Occasional line broadenings in the C and O spectra at the region of hydroxyl signals were too indistinct for quantitative analysis, but were suggestive of minute traces of water or OH bonds.

No significant differences were evident among the various specimens for the $Fe2p_{3/2}$ BE at $\sim$711.5 eV (Figure 1 a,b,c) which is characteristic of an iron oxide (13,15,16). Thus, there was no evidence of chemical reactions involving iron or changes from oxide to salt.

B. WETTABILITY

When cos Θ of each member of a homologous series of liquids on a smooth, clean, solid, low-energy surface is plotted against the surface tension γ_{LV} for each of those liquids, a straight line results; the intercept at cos $\Theta = 1$ ($\Theta = 0^{o}$) is referred to as the critical surface tension of wetting (γ_c) for that particular surface (17). Liquids whose $\gamma_{LV} \leq \gamma_c$ will spread on that surface, and those whose $\gamma_{LV} > \gamma_c$ will be nonwetting and have measurable contact angles. The concept of γ_c is equally valid for closely-packed oriented organic monolayers adsorbed on a smooth, clean, solid, high-energy surface (18). Wettability data as obtained by Θ and γ_c offer important information on the molecular constitution and molecular packing at the outermost surface layer of a bulk organic solid or an organic compound adsorbed as a close-packed and oriented monolayer on metals, metal oxides, or other high-energy surfaces.

To the extent that the contaminants which adsorb onto the steel specimen surfaces during handling are organic, they lend themselves to wetting studies. Exact chemical identification by γ_c determination is limited by random adsorption and molecular orientation. The use, however, of several diagnostic liquids of widely different chemical species, surface tensions, and molecular shapes, e.g., water ($\gamma_{LV} = 72.0$ mNm^{-1}), methylene iodide, CH_2I_2 ($\gamma_{LV} = 50.8$ mNm^{-1}), and hexadecane $C_{16}H_{34}$ ($\gamma_{LV} = 27.6$ mNm^{-1}) permits qualitative differentiation between amounts (if less than a condensed monolayer) and types of adsorbant, (i.e., hydrocarbon, fluorocarbon, etc.)

Freshly cleaned metal or metal oxide surfaces will have $\Theta = 0°$ (wetted spontaneously) by $C_{16}H_{34}$ and H_2O, and $\Theta < 20^{o}$ by CH_2I_2 (19,20); contact angles larger than that are therefore an indication of adsorbed material. Since high surface-energy surfaces readily attract adsorbents from the prevailing environment, such spontaneous wetting is usually not observed under ambient conditions with liquids whose surface tensions exceed ~ 25 mNm^{-1}. Coherence and uniformity of coverage by atmospheric contaminants is usually a measure of length of exposure, presence of substrate solid adsorption sites, and availability of adsorbate polar groups, and is reflected in the contact angles, which increase with increasing completeness of coverage.

Table IV lists contact angle values of H_2O, CH_2I_2 and $C_{16}H_{34}$ on the five sample sets. The lowest values were invariably observed on the unopened transit specimens; somewhat higher values were observed on the opened specimens. Water contact angles in the range of 55-70^{o} indicated typical hydrocarbon contamination (21), easily acquired during atmospheric exposure, as did the CH_2I_2 contact angles. Considerably higher angles were observed in the specimens processed through the entire cleaning procedures. Of the specimens subjected to single solvents only, those from the Stoddard immersion exhibited the highest contact angles (even higher than those from the entire process) and those from the Freon vapor degreaser the lowest. This suggests that additional

trace substances (which, incidentally, were also rust-inhibiting on the 52100 steel samples) were adsorbed during the cleaning steps, possibly from the L&R 222 cleaner and/or the solvents, e.g., Stoddard, employed early in the cleaning process. The steel surfaces emerging from individual dips into such solvents were often covered with gelatinous or solid residues. It is therefore possible that these cleaners added some contaminants which even the subsequent cleaning steps could not remove.

The magnitude of all the contact angles as well as the 0-5° values of hexadecane precluded the presence of adsorbed fluorocarbons on all surfaces.

H_2O and CH_2I_2 contact angles of 90° and 50°, respectively, were indicative of closely-packed $-CH_2-$ groups in the surface, and when these values are coupled with measurable, albeit low, contact angles of $C_{16}H_{34}$, they strongly suggest the additional presence of CH_3- groups. Of the specimen sets examined, that from Cherry Point exhibited the highest contact angles, followed closely by the set from Norfolk. The implications drawn from the high contact angles are in good agreement with the high C contents found by XPS for the same samples. It therefore appears that the cleaning solvents in the process tanks at Cherry Point and Norfolk, at least on the day of the measurements, contained considerable amounts of organic contaminants capable of adsorbing onto metal surfaces.

Contact angles were also measured on the NARF packaging materials, Nylon, AS Nylon and AS polyethylene (Table IV) to detect any possible additive transfer from the container to the steel surface. Contact angles on the Nylon agreed with literature values (22,23); the slowly decreasing value for H_2O is a function of H_2O interaction with the hydrophilic -NHCO- Nylon structure. Contact angles of $C_{16}H_{34}$ and CH_2I_2 on polyethylene or Nylon increased in the presence of antistatic additives, while contact angles of H_2O decreased on polyethylene because of the hydrophilicity of the antistatic additive.

Some transfer from the packaging materials to the steel surfaces is indicated, but since under the experimental conditions contact time between steel surface and packaging never exceeded 7 days (most contacts were much shorter) the effect of prolonged contact is difficult to predict.

C. INFRARED SPECTROSCOPY

1. FTIR-ATR on Steel and Germanium Surfaces

Each metal specimen was analyzed for residual surface contaminants by taking infrared spectra in the ATR mode. The spectra of the unopened transit specimens from North Island had virtually no hydrocarbon, carbonyl or ester bands, and resembled those of the glow-discharged reference specimens, thus indicating little contamination. The specimen opened to the atmosphere at North Island had more (1-2% transmission) C-H,

and traces of C-O and C=O in regions where esters absorb. Although germanium specimens processed through the cleaning line had virtually no residues, an identically processed 52100 steel specimen had a large amount of residue, whose spectra matched that of an ester-based lubricant. The largest amount of hydrocarbon C-H was observed on the specimen packaged in an AS Nylon bag. Many of the peaks in its spectrum matched those in a previously recorded spectrum of the antistatic additive known to be incorporated into the Nylon bag and were not seen in the spectra of the other samples. XPS data of the surface of a sample packaged in AS Nylon also showed nitrogen whose source might have been the AS additive, or even the Nylon itself. Specimens exposed to individual solvents picked up traces of residues absorbing in the C-H region and also had a band near 1700 cm^{-1} that can be attributed to ester C=O or to amide bands arising from certain NH structures. 1,1,1-trichloroethane in the North Island clean room left a residue suggestive of an ester oil. In all cases of individual solvent exposure, the residue did not contain any of the spectral peaks of the solvent from which it was deposited. Residues left by the several solvents appear similar and may all be due to the same type of contaminants.

ATR data on specimens from Norfolk were inconclusive due to a spectrometer computer problem and ATR data from the Norfolk cleaning system taken at an earlier date (March 1978) are described here instead. The unprocessed specimen had less residue than the one subjected to the entire cleaning cycle. The latter residue may have been deposited from the L&R watch cleaner or a residue contaminant in it in the first cleaning stage and subsequent steps in the cleaning cycle did not remove this material completely. Samples exposed to the individual solvents acquired residues, but that exposed only to the Freon VD was the cleanest of all. This suggests that the Freon VD was quite effective by itself, but that the residue, once deposited on the surface, was not easily removed even by this cleaning step.

The specimen processed through the entire cleaning cycle at Jacksonville showed virtually no difference from the reference crystal; a similarly processed sample from Pensacola had only traces of hydrocarbon, as detected by the C-H stretching intensity, which was ca 0.5% transmittance. The C-H intensity of the sample processed at Cherry Point was about twice that from Pensacola. Residues from individual solvents generally were more substantial than those from the entire cleaning processes. For example, the specimen exposed to Stoddard solvent at Jacksonville had over four times as much hydrocarbon as the reference specimen.

2. Transmission Spectra on Solvents from Process Tanks

Each sample of liquid solvent as removed from the various tanks during the NARF cleaning process was analyzed by IR transmission to ascertain the presence of contaminants. The details of the solvent spectral analysis are listed in Table V. The analysis is based on the generally accepted ability of IR to detect impurities present in liquid

phase spectra at concentrations $\geq$ 1% by comparison with known reference spectra of the pure compounds. A good match with literature spectra of ca 99 percent pure liquids is indicated in Table V.

In general, with the exceptions noted below, the solvents in use at each NARF were quite clean. The contamination in all cases was suggestive of ester or hydrocarbon lubricants; fluorocarbons or other unusual compounds were not contaminant components of the solvent spectra. The solvents from Jacksonville showed the least amounts of extraneous material, and North Island samples the next smallest. In both locations contamination occurred only in samples from the bulk supply in the vapor degreaser. Samples from Pensacola, primarily naphthas, were quite good; the Freon, however, especially in the bulk reservoir of the vapor degreaser, contained large hydrocarbon peaks. Solvents sampled at Norfolk all had a component whose bands were consistent with ester oil, strongly suggesting the presence of lubricants that were either present in the unused solvents (Table VI) or were removed by these solvents from bearings previously cleaned in these batches of solvent. These results corroborate the results of the wetting data. Solvents from Cherry Point had an unexpected carbonyl content in the naphtha while large amounts of hydrocarbon were present in all the Freon samples.

D. GRAVIMETRY

Solvents "as received from the manufacturer" and prior to use were analyzed gravimetrically; Table VI lists the concentration of contaminant non-volatile residues as ppm along with a description of their appearance. Some solvents had been drawn by the NARFs from secondary or holding tanks which were probably not free of contaminants, accounting for some of the high residue levels reported. Contaminants in the filter line may also have been contributory to these high levels. All solvents from Norfolk contained considerable quantities of oily residues, which undoubtedly contributed substantially to the subsequent steel sample contamination. Since the solvents at Cherry Point seem to be relatively pure, the heavy surface contamination found on the steel samples exposed to them was probably acquired during the cleaning of previous batches of bearings.

DISCUSSION

Three analytical procedures, i.e., wettability, AES-XPS, and FTIR, were employed in the investigation to characterize the type and level of contamination found on bearing metal surfaces exposed to various solvent combinations at the NARFs. Despite the fact that each technique sampled a relatively small portion of any one surface, the data correlated sufficiently well to warrant a high degree of confidence regardless of which method was employed.

Based on the value of $\Theta \leq 5^{\circ}$ for hexadecane (γ_{LV} = 27.6 mNm^{-1} at 20°C) for most specimens, γ_c of the most prevalent adsorbate can be estimated at 25-30 mNm^{-1}. Barring chemical reaction or hydrolysis on

deposition, a contaminant hydrocarbon film would have a γ_c close to its own γ_{LV}. Values of 25-30 mNm^{-1} for γ_c or γ_{LV} include substances that are mostly hydrocarbon with the possible presence of some polar groups. Likely contaminants in these studies would be lubricants or their degradation products from prior processing in the same solvent batches. A typical formulated mixed polyester-diester instrument oil, MIL-L-81846, has a surface tension of 25.5 mNm^{-1} and an unformulated diester base oil, bis-(2-ethylhexyl)-sebacate, has a γ_{LV} of 31.1 mNm^{-1}; such contaminant possibilities are therefore not inconsistent with the data. The contact angle values of water and methylene iodide were either below or approaching the values expected for a close-packed hydrocarbon surface. It thus appears that hydrocarbon-type contaminants predominate at the outermost surface, especially at less than monolayer coverage.

A rough correlation can be made of wettability data, as a measure of carbon contamination, with the intensity of the XPS carbon signal at a BE of 285.0 eV, the characteristic energy for the C-C bond. Figure 2 shows such a correlation when the contact angles $(\theta)_N$ of water (Table IV) are plotted versus the normalized carbon intensity I_C^N (Tables III a-e). The curves increase gradually from the theoretical zero point for θ and I_C^N to a coverage of about 0.4 I_C^N (0.35 for North Island, 0.55 for Cherry Point), which approaches the H_2O θ of 94^o for a closely-packed $-CH_2-$ surface, such as polyethylene. Since no such close-packing can be achieved by random contamination, the curves either reach linearity or descendance at a θ smaller than 94^o. If we assume that a I_C^N of $\sim$ 0.4-0.5 corresponds to a complete, albeit randomly oriented, monolayer, $I_C^N > 0.5$ must reflect increasing multilayer coverage, also in random molecular orientation. The decreasing water contact angles at $I_C^N >$ 0.5 may then be ascribed to either: 1) polar interaction of water with polar sites created in increasing numbers at the outermost surface, or 2) slippage of the small H_2O molecules through larger molecular interstices. Whereas XPS and AES sample each element to a depth of $\sim 30\text{Å}$, contact angles are sensitive only to the constitution of the outermost surface layer; a larger C intensity in XPS is therefore the result of a thicker C overlayer, and not a closer-packed array of C atoms, as witnessed by the non-increasing contact angles.

Correlation can also be obtained between infrared ATR results, again as a measure of hydrocarbon contamination, with the XPS carbon intensity signal at a BE of 285.0 eV. Such a correlation is shown in Figure 3, where the data from the North Island steel specimens, represented as intensities of the 2920 cm^{-1} C-H stretching frequency (in absorbance units) are plotted versus the normalized carbon intensities I_C^N (Table IIIa). A reasonable correlation is seen between the XPS hydrocarbon fraction and the FTIR/ATR hydrocarbon stretch intensity. The inherent error in obtaining quantitative information from ATR data is large, and absorbance values cannot be determined with accuracy unless a quantitative calibration with the compound under study is made. Since the residues studied here were of species not positively identified, a calibration was not possible.

SUMMARY

Results to date of the investigation of the effect of NARF bearing cleaning practices on the surface chemistry and contamination of bearing surfaces are summarized as follows:

1. Wettability, X-ray photoelectron and Auger electron spectroscopies (XPS and AES) and Fourier Transform Infrared (FTIR) analysis were employed as analytical tools to characterize 52100 and 440C bearing steel reference surfaces.

2. Special packaging, devised to contain the glow-discharged reference surface test specimens, protected them during transportation from all but negligible traces of atmosphere contamination. Subsequent exposure of the specimens to NARF bearing cleaning area environments resulted in a minor increase of atmospherically-born contaminants (C, S, Cl, N); contamination levels varied somewhat among the NARFs.

3. Reference specimens were exposed to the routine solvent-cleaning procedure of each NARF (except for Alameda whose system was down). Contamination levels increased measurably over the reference surfaces. One series of runs was performed at the NARF on a randomly-chosen day, so that the periods since individual solvents had been recycled or replaced differed; this may be reflected in the different contamination levels found at these facilities on the treated surfaces. The order of increasing residues was North Island ≈ Jacksonville < Norfolk ≈ Pensacola. Although samples from Cherry Point showed the highest contamination levels, ranking with the other NARFs is not justified since that facility does not deal with and is not equipped to properly handle miniature bearings.

4. Contamination of specimen surfaces exposed to individual solvents at each NARF varied considerably. Large levels of carbonaceous residues were acquired from the ultrasonic Freon bath and trichloroethane spray at Norfolk, one naphtha tank at Pensacola and all solvents at Cherry Point. Generally the least contamination was acquired from Freon vapor degreasers, even though the residual solvent had large hydrocarbon contents.

5. Residual contaminants on the specimen surfaces were primarily hydrocarbons with small amounts of ester linkages, not inconsistent with instrument lubricants (or their degradation products) in Navy use. Additives incorporated into various solvents by suppliers probably also contributed to the residues found. Generally, the greater the surface contamination of the specimens, the less wettable they were. Some contaminants on 52100 steel were found to be rust inhibiting.

6. There was no clear evidence of chemical reaction between the iron oxide surface and the overlaying contaminants, as demonstrated by the unaltered binding energies of the iron XPS spectra, and the oxygen XPS spectra which remained characteristic of an oxide.

7. Test specimens transported from the NARFs to NRL in antistatic Nylon or polyethylene packaging showed little evidence of contamination from the antistatic additive, possibly due to the relatively short period of contact and minimal amount of handling.

CONCLUSIONS AND FUTURE WORK

1. Surface chemical properties of contaminants and/or additives laid down on reference simulated bearing surfaces undergoing solvent-cleaning at the various NARFs are such as to be detrimental to wetting by lubricants in actual bearings. This effect can lead to lubricant starvation and ultimate bearing failure. Beneficial spin-offs of these uncontrolled surface residues, e.g., non-rusting of 52100 steels, are considered of less significance than the detrimental effects.

2. Though residue levels on the reference surfaces after solvent treatment by the NARFs differed, it is likely the relative ranking would change whenever the test sequences were repeated. This assumption is based on the premise that the condition of the solvents in the tanks varies from day-to-day. Although NARF personnel involved in this work were uniformly diligent in carefully following their local engineering practices, occasional human error could result in bearings with less than acceptable clean surfaces.

3. The next phase of this study will include placing well-defined chemical contaminants on the reference surfaces and determining their degree of removal by current solvent treatments. The study will be expanded to include the other DOD facilities concerned with precision miniature bearings, and a bearing vendor. Based on the results obtained with reference surfaces, the final phase of this study will be to examine the effect of solvent cleaning of actual bearing surfaces.

4. The present study presents only one aspect, albeit an important one, of how prior treatment of bearings contributes to acceptable bearing surfaces. Other treatments, e.g., ion implantation, chemical soaking, etc., are of at least equal significance as regards bearing life and performance.

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Appendix I

INSTRUMENT BEARING CLEANING MATERIALS

Military Specification Materials

VV-L-800	Light Petroleum Oil
MIL-TT-N-95	Naphtha, Aliphatic
P-D-680 (Type I)	Dry Cleaning Solvent (Stoddard Solvent)
MIL-C-81302 (Type I)	Cleaning Compound, Solvent, 1,1,2-Trichloro-1,2,2-Trifluoroethane (Ultra-Clean Particulates <10 ppm) Freon
MIL-C-81302 (Type II)	Cleaning Compound, Solvent, 1,1,2-Trichloro-1,2,2-Trifluoroethane (Standard, Some Particulates) Freon
MIL-T-81533	1,1,1-Trichloroethane (Methyl Chloroform) Inhibited
MIL-C-1985	Carbon Remover
MIL-C-15074	Fingerprint Remover (Stoddard + Amine + Corrosion Inhibitor)

Proprietary Materials

L&R 222	Cleaning Solution, Watch L&R Manufacturing Co. (FSCM 34560) 577 Elm St., Kearny, NJ 07032

Appendix IIa

CLEANING PROCESS AT NARF A (June 2, 1978)

CLEANER	METHOD	TIME (min.)	FOLLOW-UP	CLEANER CHANGE	FILTER (μ)	FILTER CHANGE
(1) L&R 222	Ultrasonic	10	Drain	Every 2 days	None	None
(2) Stoddard	Agitated Soak	10	Drain	Daily	10	Weekly
(3) Freon	Agitated Soak	10	Drain	Weekly	None	None
(4) Freon	Vapor Degrease	10		Daily	10	Monthly
(5) Oven (no cleaner)	Dry at 98°F	5				
Clean Room (1,000):						
(6) Freon	Ultrasonic	3-4		Filtered each use		
(7) Trichloroethane	Spray Gun	~ 1	Dry with forced air	Continuous; 1x use	5	
(8) Freon	Vapor Degrease	3-4		Weekly	10	Monthly

Appendix IIb

CLEANING PROCESS AT NARF B (July 19, 1978)

	CLEANER	METHOD	TIME (min.)	FOLLOW-UP	CLEANER CHANGE	FILTER (μ)	FILTER CHANGE
(1)	Stoddard	Spray	~ 1	Dry with N_2 Jet	Continuous, 1x use	1	Daily
(2)	L&R 222	Ultrasonic	2-5	Spray with Stoddard; Dry with N_2 Jet	Every Other Day	None	None
(3)	Stoddard	Agitated Soak	5	Spray with Freon; Dry with N_2 Jet	Weekly	Continuous; 10	Weekly
(4)	Freon	Ultrasonic	2-5	-	Daily	None	None
(5)	Trichloroethane (inhibited <5%)	Spray	~ 1	-	Continuous; 1x use	1	Daily
(6)	Freon	Vapor Degrease	10	-	Drain Clean; Change every 2 weeks	None	None
(7)	Oven (Adjoining room)	Dry at ~ 120°F	5-10	(May remain stored for several days)			
	Spray Booth N_2				None	1	Daily

Appendix IIc

CLEANING PROCESS AT NARF C (September 8, 1978)

CLEANER	METHOD	TIME (min.)	FOLLOW-UP	CLEANER CHANGE	FILTER (μ)
(1) Stoddard	Soak with Brushing	Varies	Drain	Several Times per Day	0.22, Triply Filtered
(2) L&R 222	Ultrasonic	7	Drain, spray with Freon over VD tank	Every Other Day	None
(3) Freon	Vapor Degrease	1		Every 2 Weeks	0.22, in-line Filter
(4) Stoddard	Soak; occasional shake	5	Drain	Everyday	0.22, Triply Filtered
(5) Freon (adjoining room)	Ultrasonic	2		2-3 Times Weekly	0.22, in-line Filter
(6) Trichloroethane (inhibited)	Spray	1		Continuous; 1x use	Sonogen Filter
Original Room:					
(7) Freon	Vapor Degrease (same tank as (3))	1	Vacuum Off Excess	Every 2 Weeks	0.22, in-line Filter
Adjoining Room:					
(8) Oven	Dry at 110°F		May Remain Stored		

Appendix IId

CLEANING PROCESS AT NARF D (September 11, 1978)

	CLEANER	METHOD	TIME (min.)	CLEANER CHANGE	FILTER	FILTER CHANGE
(1)	Naphtha (5 pots sequentially)	Soak	1/2-1 ea	Daily	0.45 µm millipore	Daily
(2)	Oil (hot)	Soak	10			
(3)	Naphtha	Dip, Rinse	-		0.45 µm	Daily
(4)	Freon	Ultrasonic	2-3	Daily		Daily
(5)	Freon	Ultrasonic	2-3	Daily		Daily
(6)	Naphtha	Dip, Rinse	-			
	In Clean Room (10,000):					
(7)	Trichloroethane	Spray Then dry with N_2 gun	~ 1	Continuous, 1x use		
(8)	Oven	Dry at 110°F	Remains Stored			

Appendix IIe

CLEANING PROCESS AT NARF E (September 28, 1978)

CLEANER	METHOD	TIME (sec.)	FOLLOW-UP	CLEANER CHANGE
(1) Trichloroethane	Vapor Degrease	15		Every 2 Weeks
(2) Stoddard (several tanks sequentially)	Agitated Soak	40	Air Blast	Every 2 Weeks, Filter Change
(3) H_2O, hot	Hot Pressure Spray	60	Air Blast	
(4) Isopropyl Alcohol #1	Dip	25		
(5) Isopropyl Alcohol (+ immunol) #2 1 oz/gal alc	Dip	25		
(6) Freon	Ultrasonic	10		Every 2 Weeks; Dump when Contaminated
(7) Freon (same tank)	Vapor Degrease	10		Every 2 Weeks
Clean Room (100,000):				
(8) Fingerprint Remover	Agitated Soak	20		Every 2 Weeks
(9) Stoddard	Agitated Soak	60		Every 2 Weeks
(10) Stoddard (final tank)	Agitated Soak	60		Every 2 Weeks
(11) Oven (120°F)	Stored			

Appendix III

SENSITIVITY CORRECTION AND NORMALIZATION OF XPS INTENSITIES

Semiquantitative elemental ratios can be obtained by correcting each observed XPS peak intensity, I_i, according to the relative sensitivities, which is dominated by the cross-section for X-ray absorption of the respective subshell (24). Corrections were neglected for the electron mean free path energy dependence which are in the order of about 20%. Furthermore, the Fe lineshape does not provide a clearly defined intensity and there is some systematic uncertainty in the manner in which I_{Fe} can be measured. Within these limits, the normalized relation I_i^N for each element can then be calculated by

$$I_i^N = \frac{I_i S_i^{-1}}{\Sigma\, I_i S_i^{-1}}$$

where S_i represents the elemental subshell sensitivity factor and $\Sigma\, I_i S_i^{-1}$ represents the corrected sum of the three major contributing elements, Fe, O and C. Using the sensitivity factor S_i for the carbon 1s subshell as unity and adjusting for the X-ray energy of 1487 eV (25), S_i for the three elements are $C_{1s} = 1.00$, $Fe_{2p3/2} = 10.8$, and $O_{1s} = 2.9$. S_i of $F_{1s} = 4.4$ was included in the one $\Sigma\, I_i S_i^{-1}$ where fluorine also contributed a significant signal (Table II b).

Comparison of I_O^N and I_C^N to I_{Fe}^N yields approximate stoichiometric surface elemental ratios. Epitaxial iron oxide observed in an independent study (26) yielded I_O^N/I_{Fe}^N ratios of 4.2-5.0, the large ratios probably due to the uncertainties inherent in these measurements. The I_O^N/I_{Fe}^N ratios in the 52100 and 440C steel surfaces of approxminately 5.5 and 8.0, respectively, were to a major part due to the iron oxide constitution. Since in the present report all surface constituents, except Fe, O and C have been neglected in the calculation, the, I_O^N/I_{Fe}^N ratio will necessarily be even greater; e.g., the ratio of 8.0 in 440C steel, which contains larger amounts of Cr, is a clear indication that significant amounts of O are due to chromium oxide.

Table I

STEEL SPECIMEN SAMPLING PLAN FOR EACH NARF

I. Transit Control:

a) Remain unopened and returned

b) Opened to NARF atmosphere and returned

II. Entire Cleaning Cycle:

a) Returned in NRL container

b) Returned in NARF container (PE or Nylon bag)

III. Individual Solvent Treatment:

Stoddard

Freon Ultrasonic

Freon Vapor Degrease

Trichloroethane

Other

Table IIa

RELATIVE ELEMENTAL INTENSITIES ON STEEL SURFACES
(Normalized to Fe = 10; and Uncorrected for Sensitivities)

NARF A

SPECIMEN	AES, (INTENSITY)					XPS, (INTENSITY)						
	S	Cl	N	C	O	S	N	C	O	F	Zn	Ba
Unopened	0.5	1.1	-	1.1	31.0	0.3	-	0.9	15.2			
Opened	3.0	3.8	-	15.2	40.0	-	-	4.2	14.2			X
Cleaned	0.5	1.1	-	4.1	>38	0.1	-	2.8	16.1			X
Cleaned (AS Nylon)(1)	0.5	0.7	0.5	4.6	40.0	0.1	0.2	2.2	15.6			
Freon US(2)	1.4	0.4	-	1.2	36.8	0.2	0.1	1.6	15.6			
Trichloroethane	0.9	0.3	-	1.7	20.6	-	-	1.5	16.8			

(1) NARF packaging material: antistatic Nylon

(2) US: Ultrasonic

Table IIb

RELATIVE ELEMENTAL INTENSITIES ON STEEL SURFACES

(Normalized to Fe = 10; and Uncorrected for Sensitivities)

NARF B

SPECIMEN	AES, (INTENSITY)						XPS, (INTENSITY)						
	S	Cl	N	C	O	Zn	S	N	C	O	F	Zn	Ba
Unopened	0.7	0.8	-	0.5	38.0	X	0.4	-	1.0	16.7	-	-	-
Unopened	0.6	1.9	0.1	1.3	37.5	X	0.4	0.4	1.2	17.3		X	
Opened	7.6	4.7	0.3	0.8	36.8		0.3	0.3	1.0	16.2		X	
Cleaned	0.8	0.8	0.5	5.9	45.5		0.2	0.5	4.4	17.1		X	
Cleaned	1.5	1.2	0.5	5.7	42.0		0.1	0.5	3.1	15.0			
Cleaned (AS PE)(1)	0.6	0.2	0.5	5.9	24.9		0.1	0.4	3.5	14.9		X	
Cleaned (AS PE)(1)	0.5	0.5	0.4	6.2	35.7		0.1	0.3	3.8	16.6		X	
Stoddard	0.1	1.8	0.5	5.1	34.4		0.2	0.3	3.3	16.7		X	
Freon US(2)	1.5	2.0	1.5	23.3	26.7		0.4	1.2	18.5	18.5			
Trichloroethane	2.7	2.7	0.7	26.7	28.9		0.5	-	32.5	20.0			
Freon VD(2)	2.2	2.9	0.1	21.8	30.9		0.4	1.1	15.5	17.5			
Freon VD(2)	1.2	2.0	0.8	5.4	32.9		0.2	0.7	1.8	14.4	8.9		

(1) NARF packaging material: antistatic polyethylene

(2) US: ultrasonic; VD: vapor degrease

Table IIc

RELATIVE ELEMENTAL INTENSITIES ON STEEL SURFACES

(Normalized to Fe = 10; and Uncorrected for Sensitivities)

NARF C

SPECIMEN	AES, (INTENSITY)						XPS, (INTENSITY)							
	S	Cl	N	C	O	Zn	Cl	S	N	C	O	F	Zn	Ba
Unopened	1.8	1.4	0.3	1.6	41.4	X	-	0.3	0.2	1.0	15.5	-	X	-
Opened	2.0	2.8	0.4	2.2	43.7	X	-	0.3	0.1	1.3	15.8	-	-	-
Cleaned	0.3	1.2	0.5	2.9	36.4	-	-	Trace	0.4	2.1	15.3	-	-	-
Cleaned	0.6	4.6	0.6	4.8	39.2	-	-	0.3	0.2	2.1	14.7	-	-	-
Cleaned (AS Nylon)(1)	0.7	1.7	0.8	7.1	34.1	-	-	Trace	0.3	3.5	17.0	-	Trace	-
Stoddard	0.8	2.5	0.8	9.1	38.7	X	-	0.4	0.6	4.8	18.6	-	Trace	-
Freon US(2)	0.9	1.8	0.5	5.5	36.3	X	-	Trace	0.2	2.5	16.7	-		
Trichloroethane	1.2	7.0	1.7	8.3	34.3	-	0.3	0.4	1.0	5.3	17.1	0.4	-	-
Freon VD(2)	1.0	3.8	0.8	4.5	34.0	-	-	0.2	0.5	1.9	15.8	0.2	-	-

(1) NARF packaging material: antistatic Nylon

(2) US: ultrasonic; VS: vapor degrease

Table IId

RELATIVE ELEMENTAL INTENSITIES ON STEEL SURFACES

(Normalized to Fe = 10; and Uncorrected for Sensitivities)

NARF D

SPECIMEN	AES, (INTENSITY)						XPS, (INTENSITY)						
	S	Cl	N	C	O	Zn	S	N	C	O	F	Zn	Ba
Unopened	1.9	0.8	0.3	3.2	36.1	-	0.5	0.1	1.7	14.8	-	-	-
Opened	2.4	0.6	0.4	6.4	36.8	-	0.3	0.3	2.0	14.0	0.1		X
Cleaned	3.0	3.4	-	7.6	36.8	-	0.5	0.2	4.6	16.3	-	-	-
Cleaned (Nylon) (1)	2.7	3.8	0.3	8.8	39.0	X	0.3	0.3	4.6	16.5	-	-	-
Naphtha 1	3.1	3.1	0.6	14.1	35.0	-	0.6	0.4	6.7	16.0	-	-	X
Naphtha 2	0.5	0.4	0.8	22.0	32.0	-	0.6	0.6	13.1	16.9	-	-	-
Freon US 1 (2)	1.1	1.1	0.4	6.7	35.6	-	0.2	0.4	3.8	16.3	0.4	-	-
Freon US 2 (2)	0.6	5.0	0.8	5.6	32.0	-	0.2	0.5	2.9	15.5	0.8	-	-
Naphtha 3	1.1	3.8	1.1	6.0	32.4	X	0.1	0.9	3.3	14.0	-	-	-
Trichloroethane	0.8	4.1	1.0	8.0	32.8		0.1	0.6	4.3	16.5	-	-	

(1) NARF packaging material: Nylon

(2) US: ultrasonic

Table IIe

RELATIVE ELEMENTAL INTENSITIES ON STEEL SURFACES

(Normalized to Fe = 10; and Uncorrected for Sensitivities)

NARF E

SPECIMEN	AES, (INTENSITY)						XPS, (INTENSITY)						
	S	Cl	N	C	O	Zn	S	N	C	O	F	Zn	Ba
Unopened	0.5	0.9	0.4	4.0	41.7		0.2	0.4	2.0	22.0			
Opened	-	-	-	-	-		-	0.3	1.8	21.5			
Cleaned	1.4	0.8	0.5	26.4	45.9		0.2	-	14.2	25.0	-	-	X
Freon US(1)	1.7	0.6	0.3	21.7	53.7		0.3	0.4	12.1	21.3			
Trichloroethane VD(1)	-	-	-	-	-		0.3	-	11.4	23.1	2.3		
Fingerprint Rem.	-	-	-	-	-		0.1	0.4	16.2	25.5	-	-	
Stoddard (final)	0.5	1.0	0.3	11.1	36.3		-	-	8.8	23.3	-	-	

(1) US: ultrasonic; VD: vapor degrease

Table IIIa

RELATIVE SURFACE ABUNDANCE OF IRON, OXYGEN AND CARBON (XPS)

(Corrected for Sensitivities, Appendix III)

NARF A

SPECIMEN	Fe	O		C	
	I^N_{Fe}	I^N_O	I^N_O/I^N_{Fe}	I^N_C	I^N_C/I^N_{Fe}
Unopened	0.13	0.74	5.6	0.13	0.9
Opened	0,09	0.49	5.2	0.42	3.6
Cleaned	0.11	0.61	5.8	0.31	3.0
Cleaned (AS Nylon)(1)	0.11	0.64	5.9	0.26	2.4
Freon US(2)	0.12	0.69	5.9	0.20	1.7
Trichloroethane	0.11	0.71	6.3	0.18	1.7

(1) NARF packaging material: antistatic Nylon

(2) US: ultrasonic

Table IIIb

RELATIVE SURFACE ABUNDANCE OF IRON, OXYGEN AND CARBON (XPS)

(Corrected for Sensitivities, Appendix III)

NARF B

SPECIMEN	Fe	O		C		F	
	I^N_{Fe}	I^N_O	I^N_O/I^N_{Fe}	I^N_C	I^N_C/I^N_{Fe}	I^N_F	I^N_F/I^N_{Fe}
Unopened	0.12	0.75	6.2	0.13	1.1		
Unopened	0.11	0.73	6.4	0.15	1.4		
Opened	0.12	0.74	6.0	0.13	1.1		
Cleaned	0.08	0.53	6.4	0.39	4.7		
Cleaned	0.10	0.58	5.6	0.32	3.1		
Cleaned (AS PE)(1)	0.10	0.54	5.5	0.37	3.8		
Cleaned (AS PE)(1)	0.09	0.55	6.2	0.37	4.2		
Stoddard	0.09	0.57	6.2	0.33	3.6		
Freon US(2)	0.04	0.25	6.9	0.72	20.0		
Trichloroethane	0.02	0.17	7.4	0.81	34.8		
Freon VD(2)	0.04	0.27	6.5	0.69	16.7		
Freon VD(2)	0.10	0.51	5.4	0.19	1.9	0.21	2.2

(1) NARF packaging material: antistatic polyethylene

(2) US: ultrasonic; VD: vapor degrease

Table IIIc

RELATIVE SURFACE ABUNDANCE OF IRON, OXYGEN AND CARBON (XPS)

(Corrected for Sensitivities, Appendix III)

NARF C

SPECIMEN	Fe	O		C	
	I^N_{Fe}	I^N_O	I^N_O/I^N_{Fe}	I^N_C	I^N_C/I^N_{Fe}
Unopened	0.13	0.74	5.7	0.13	1.0
Opened	0.12	0.71	5.8	0.17	1.4
Cleaned	0.11	0.64	5.7	0.33	2.5
Cleaned	0.11	0.63	5.5	0.26	2.3
Cleaned (AS Nylon)(1)	0.09	0.57	6.3	0.34	3.8
Cleaned (AS Nylon)(1)	0.09	0.56	6.2	0.35	3.8
Stoddard	0.08	0.53	6.9	0.39	5.1
Freon US(2)	0.10	0.63	6.1	0.27	2.6
Trichloroethane	0.08	0.49	6.4	0.44	5.8
Freon VD(2)	0.11	0.66	5.8	0.23	2.0

(1) NARF packaging material: antistatic Nylon

(2) US: ultrasonic; VD: vapor degrease

Table IIId

RELATIVE SURFACE ABUNDANCE OF IRON, OXYGEN AND CARBON (XPS)

(Corrected for Sensitivities, Appendix III)

NARF D

SPECIMEN	Fe	O		C	
	I^N_{Fe}	I^N_O	I^N_O/I^N_{Fe}	I^N_C	I^N_C/I^N_{Fe}
Unopened	0.12	0.66	5.5	0.22	1.8
Opened	0.12	0.62	5.2	0.26	2.2
Cleaned	0.08	0.50	6.1	0.41	4.9
Cleaned	0.07	0.49	6.7	0.44	6.0
Cleaned (Nylon)(1)	0.08	0.51	6.2	0.41	5.0
Cleaned (Nylon)(1)	0.09	0.48	5.7	0.43	5.1
Naphtha 1	0.07	0.42	6.0	0.51	7.2
Naphtha 2	0.05	0.29	6.3	0.66	14.2
Freon US 1(2)	0.09	0.54	6.1	0.37	4.1
Freon US 2(2)	0.10	0.58	5.8	0.37	3.2
Naphtha 3	0.10	0.53	5.2	0.37	3.6
Trichloroethane	0.09	0.52	6.1	0.39	4.6

(1) NARF packaging material: Nylon

(2) US: ultrasonic

Table IIIe

RELATIVE SURFACE ABUNDANCE OF IRON, OXYGEN AND CARBON (XPS)

(Corrected for Sensitivities, Appendix III)

NARF E

SPECIMEN	Fe	O		C	
	I^N_{Fe}	I^N_O	I^N_O/I^N_{Fe}	I^N_C	I^N_C/I^N_{Fe}
Unopened	0.09	0.72	8.2	0.19	2.2
Opened	0.09	0.73	8.1	0.18	2.0
Cleaned	0.04	0.36	9.4	0.60	15.5
Cleaned	0.04	0.37	9.3	0.60	15.2
Trichloroethane VD[1]	0.05	0.39	8.6	0.56	12.4
Freon US[1]	0.05	0.36	8.0	0.59	13.1
Fingerprint Rem.	0.04	0.34	9.6	0.63	17.6
Stoddard (final)	0.04	0.37	9.3	0.60	15.2

(1) US: ultrasonic; VD: vapor degrease

Table IIIf

RELATIVE SURFACE ABUNDANCE OF IRON, OXYGEN AND CARBON (XPS)

(Corrected for Sensitivities, Appendix III)

REFERENCE SURFACES (Glow Discharged)

SPECIMEN	Fe	O		C	
	I^N_{Fe}	I^N_O	I^N_O/I^N_{Fe}	I^N_C	I^N_C/I^N_{Fe}
52100	0.14	0.74	5.2	0.11	0.8
52100	0.14	0.74	4.6	0.10	0.7
52100	0.14	0.78	5.5	0.08	0.6
52100	0.14	0.77	5.5	0.09	0.6
440 C	0.10	0.78	8.0	0.13	1.3
440 C	0.09	0.73	7.8	0.18	1.9
440 C	0.11	0.78	7.3	0.11	1.1

Table IV

WETTABILITY OF STEEL SURFACES

SPECIMEN	CONTACT ANGLE (°)														
	H_2O					CH_2I_2					$C_{16}H_{34}$				
NARF	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
Unopened	56	40	-	-	53	37	37	-	-	40	spr	spr	-	-	spr
Opened	56	48	-	-	-	42	38	-	-	-	spr	spr	-	-	-
Cleaned	72	91	78	77	89	42	48	46	50	49	spr	< 5	spr	< 5	spr
Cleaned (Packaged)(1)	73	85	85	67	-	43	54	50	45	-	spr	< 5	spr	< 5	-
Stoddard	-	85	88	56	82	-	55	54	50	48	-	19	8	spr	spr
Freon US(2)	40	90	72	52	83	38	50	43	39	48	spr	< 5	< 5	spr	< 5
Trichloroethane	63	74	59	60	68	42	40	42	45	45	spr	< 5	< 5	spr	spr
Freon VD(2)	-	88 46	44	-	-	-	48 29	39	-	-	-	spr	spr	-	-

(1) Packaging material:

Nylon: $\theta_{H_2O} = 66^\circ$ (decreases, interacts); $\theta_{CH_2I_2} = 31^\circ$; $\theta_{C_{16}H_{34}} =$ spr

Nylon, AS: $\theta_{H_2O} = 60^\circ$; $\theta_{CH_2I_2} = 52^\circ$; $\theta_{C_{16}H_{34}} = 20^\circ$

Polyethylene, AS: $\theta_{H_2O} = 35^\circ$; $\theta_{CH_2I_2} = 57^\circ$; $\theta_{C_{16}H_{34}} = 15^\circ$

(2) US: ultrasonic; VD: vapor degrease

Table V

EXTRANEOUS COMPONENTS IN SOLVENTS FROM PROCESS TANKS

SOLVENT	(FTIR Transmission)[1]				
	NARF A	NARF B	NARF C	NARF D	NARF E
Stoddard	H_2O (trace)	C=O, C-O-R (ester)	> 99% pure	-	C=O, C-O-R (ester)
Freon US[2]	> 99% pure	C-H, C=O (ester)	C-H (trace)	> 99% pure	-
Freon VD[2]	C-H	C-H	C-H	C-H (large)	C-H
Trichloroethane	C=O	C=O, C-H (ester)	> 99% pure	> 99% pure	-
Naphtha 1	-	-	-	C-H (trace)	-
Naphtha 2	-	-	-	> 99% pure	-

(1) C-H: hydrocarbon: absorbance at 3000-2800 cm^{-1}
C=O: absorbance at 1750-1650 cm^{-1} (ester or acid)
C-O-R: absorbance at 1400-1100 cm^{-1}
H_2O: broad absorbance near 3500 cm^{-1}
ester: C=O, C-H, and C-O-R

(2) US: ultrasonic, VD: vapor degrease

Table VI

RESIDUES IN SOLVENTS AS RECEIVED FROM MANUFACTURER

NARF	SOLVENT	TREATMENT	MANUFACTURER	RESIDUE (ppm)	REMARKS
A	Stoddard	-	Peninsula Oil	100	Oily residue
	Freon	-	Allied Chem.	1	No visible residue
B	Stoddard	-	Unknown	110	-
	Freon	-	Du Pont	90	Oily residue
	Freon	filtered	Du Pont	87	Low visc. oily residue
	Trichloroethane (inhibited)	filtered	Dow Chem.	352	Oily residue
C	Stoddard	-	BWI Plastics	60	Oily residue
	Freon	-	Du Pont	9	-
	Trichloroethane	-	BWI Plastics	5	-
D	Naphtha	-	Phipps Prod.	3	No visible residue
	Naptha	filtered	Phipps Prod.	19	More volatile than Naphtha
	Freon	-	Allied Chem.	4	Oily and particulate
	Freon	filtered	Allied Chem.	5	-
	Trichloroethane	-	Am. Writing Ink	13	Yellow oily residue
	Trichloroethane	filtered	Am. Writing Ink	13	Yellow oily residue
E	Stoddard (initial)	-	AMSCO, Union Oil	8	Oily residue
	Stoddard (final)	-	AMSCO, Union Oil	22	Yellow oily residue
	Freon	-	Du Pont	30	Oil and fine particulate residue
	Trichloroethane (inhibited)	-	Phipps Prod.	20	Oil and fine particulate residue

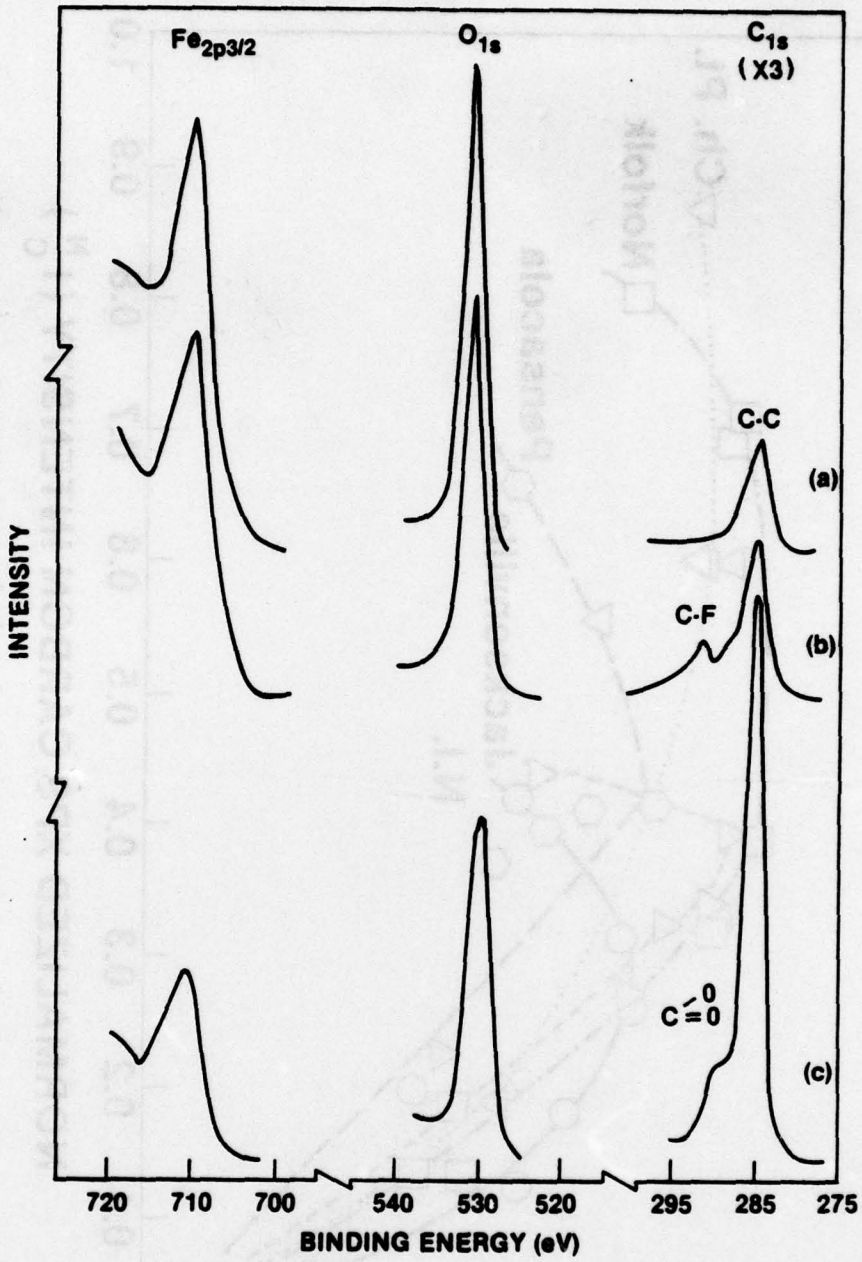

Fig. 1 — Relative intensities and energy shifts of Fe, O, and C XPS spectra after various exposures

a) NARF B, unopened transit
b) NARF B, freon vapor degrease; note C-F peak and suppressed O intensity
c) NARF E, entire cleaning; note large C intensity, $C^{=O}_{-O}$ peak, suppressed intensity and energy shift of O, and suppressed intensity of Fe

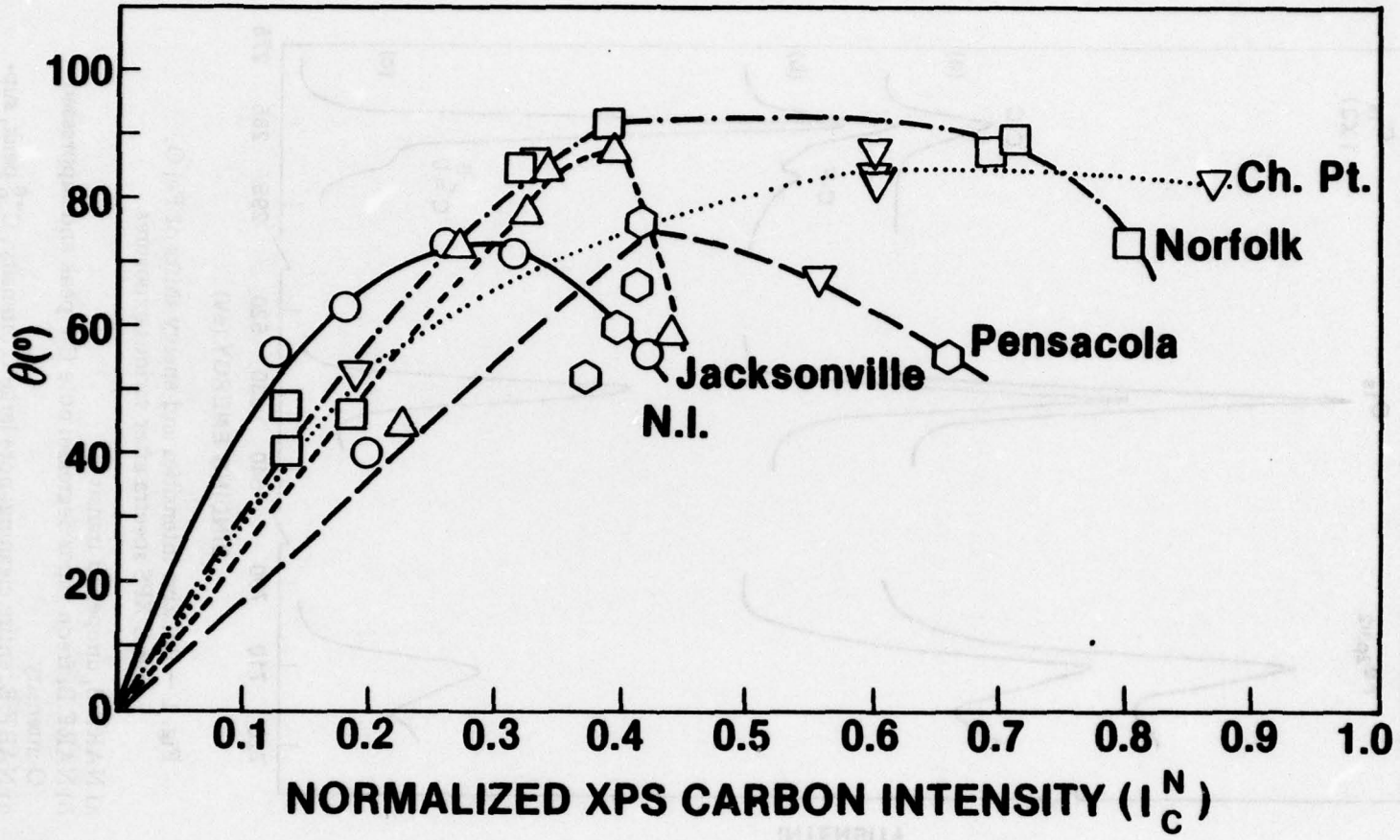

Fig. 2 — Relation of water contact angle to hydrocarbon coverage

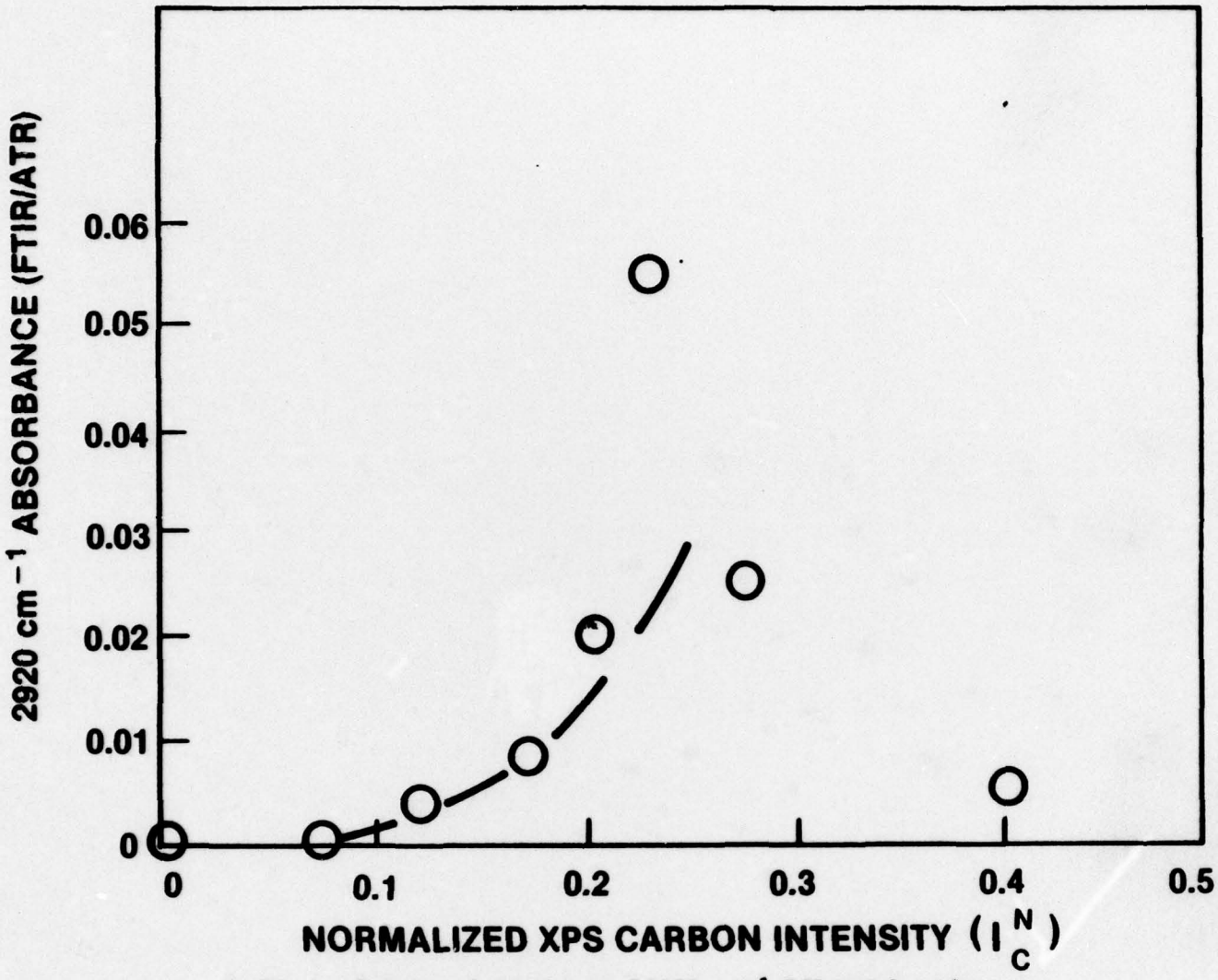

Fig. 3 — Relation of absorbance of 2920 cm^{-1} C-H stretch mode (FTIR/ATR) to hydrocarbon coverage (NARF B)